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The effects of carbon nanotube reinforcement on adhesive joints for naval applications

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NAVAL POSTGRADUATE SCHOOL

MONTEREY, CALIFORNIA

THESIS

THE EFFECTS OF CARBON NANOTUBE REINFORCEMENT OF ADHESIVE JOINTS FOR NAVAL APPLICATIONS

by

Garrett L. Burkholder

December 2009

Thesis Advisor: Young W. Kwon
Second Reader: Randall D. Pollak

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13. ABSTRACT (maximum 200 words)

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It was demonstrated that an adhesive joint with greater strength than a similarly constructed scarf joint can be created. It was further shown that the addition of MWNTs to the adhesive increased the Mode II fracture strength of the adhesive for a steel-composite and composite-composite joints. It was also shown that the fracture path shifted from through the adhesive when no nanotubes were present to between the adhesive and metal or composite interface with the addition of nanotubes.

The concentration, diameter, length and functionalization of the MWNTs added to the adhesive played a significant role in the strength of the joint. Not all nanotubes improved joint strength. Finally, it was determined that the distribution of the MWNTs in the adhesives impacted the ultimate strength of the bond. The functionalization of the nanotubes with a carboxyl group improved nanotube distribution in the adhesive and show significant promise for further improving the joint strength.

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THE EFFECTS OF CARBON NANOTUBE REINFORCEMENT ON ADHESIVE JOINTS FOR NAVAL APPLICATIONS

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LIST OF ACRONYMS AND ABBREVIATIONS

CNT   Carbon Nanotube

CoNap   Cobalt Naphthenate

DMA   Dimethylaniline

IR   Infared

MEKP   Methyl Ethyl Ketone Peroxide

MWNTs   Multi-walled Carbon nanotubes

NPS   Naval Post graduate School

NSWC   Naval Surface Warfare Center

SEM   Scanning Electron Microscopy

SWNTs   Single-walled Carbon Nanotubes

VARTM   Vacuum Assisted Resign Transfer Molding

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I. INTRODUCTION AND BACKGROUND

A. COMPOSITES

Almost since the development of modern composites in the late 1920s, composites have seen a continual increase in the applications in which they are used. A composite's ability to be formed into complex shapes, high strength and low weight has contributed to their growing popularity. The raw materials to produce a composite are generally more abundant than their metal counterparts. For a variety of reasons composites have also seen an increased use in naval construction [1]. One of the major challenges in ship construction is weight distribution; in particular it is becoming increasingly difficult with the advent of larger radars, and communication suites to reduce the amount of weight above the water line. Weight located high on the ship has a significant impact on ship stability and handling. Composites offer increased strength and corrosion resistance at a reduced weight compared to metal alternatives. Thus the use of composites in the super structure, above the water line, is becoming more wide spread in naval ship construction. Composite materials also significantly reduce costs over the life of the ship. This is because the effort and cost of composite preservation is significantly less than the preservation of metal alternatives over the life of the ship.

B. JOINTS

One of the challenges in using composite materials for construction is the joining of the materials, either to another composite or a non-composite. These joints are the weakest point of the composite structure because of the discontinuity of the fibers. Previous research at the Naval Postgraduate School (NPS) has been done on these joints. Susan Faulkner, showed that carbon nanotubes could be used to strengthen a scarf joint [2]. William Schultz and Joe Klopfer conducted work on the feasibility of including a metal layer in the composite matrix to enable the composite to be welded to metal structures [3, 4]. In all three bodies of research, the goal was to improve existing composite joining techniques.

An alternative to a co-cured scarf joint or a welded joint is an adhesive joint. Adhesive joints could be used in a wide variety of joint applications, composite to composite, composite to steel or even composite to aluminum. Research has shown that dispersion of single-walled carbon nanotubes (SWNTs) and alumina nanofiber can be used to improve strength characteristics of adhesively bonded joints [5].

C.   NANOTECHNOLOGY

Carbon nanotubes (CNTs) have been the subject of numerous papers and intensive research since they were discovered by Iijima in 1991 [6]. The high strength, stiffness, electrical conductivity and heat transfer properties of CNTs make them an attractive subject of research to a very broad audience. Since their discovery more papers have been written on CNTs than any other topic. Significant effort has also gone into incorporating CNTs in various materials in an attempt to transfer their unique mechanical and electrical properties to the bulk material. In fact so much work has been conducted in this area that a new class of materials known as nanocomposites has emerged.

1.   Nanocomposites

Jia et al., were among the first to create a nanocomposite [7]. A nanocomposite, like a traditional composite has two parts, a filler and the matrix. A traditional composite typically uses a fiber such as carbon fiber or fiberglass as the filler, in a nanocomposite the filler is a nanomaterial. Nanomaterial ranges in size from 1-100nm. Some examples of nanomaterial are CNTs, carbon nanofiber, and nanoparticles such as gold, silver, diamond, copper, and silicon. Of particular interest are CNT nanocomposites because of their high strength and stiffness composites they produce at relatively low CNT concentrations [8–10].

One of the significant challenges faced in the creation of a nanocomposite is the even dispersion of the nanomaterial in the matrix. In particular CNTs have a tendency to wrap around each other and not disperse in the matrix. In order to overcome this tendency several approaches have been taken. The first is to separate the CNT by mechanical means such as high shear mixing or sonication [11–13]. Surfactants have

also been used to aid in the dispersion of CNTs. More recently the focus has been on chemical functionalization of the CNTs.

2. Functionalized Carbon Nanotubes

A functionalized CNT is one in which a chemical group such as a carboxyl group or amine is bonded to the surface of the nanotube. Once the initial functionalization has taken place, frequently a carboxyl group, any number of different function groups can replace it using well established chemistry techniques. Functionalization of nanotubes provides the opportunity for CNTs to be specifically designed for a given application. Careful selection of the functional group can significantly improve chemical bonding between the CNT and matrix and thus strength transfer from the CNT to the bulk matrix. Chemical functionalization of both multi-walled carbon nanotubes (MWNTs) and single walled carbon nanotubes (SWNTs) has been shown to improve the mechanical and electrical properties of nanocomposites with a wide variety of matrixes [14–18].

D. OBJECTIVE OF RESEARCH

Although significant effort has gone into studying various composite joining techniques for naval applications as well as the development of nanocomposites, to date there has not been an effort to use a nanocomposite to improve joint strength for a naval application. This research will focus on this area. Several basic questions will be addressed. First, can an adhesive joint be produced with the same or greater strength than a co-cured scarf joint? Second, can an adhesive joint's strength be improved by incorporating MWNTs into the adhesive using a basic mechanical mixing technique? Third, can better dispersion of the nanotubes in the adhesive and thus greater adhesive strength be achieved by using a functionalized MWNT? Finally, what effect does changing the diameter, length or structure of the MWNTs have on adhesive strength?

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II. EXPERIMENTAL

A. MATERIAL SELECTION

In general material selection was based on recommendations received from Naval Surface Warfare Center (NSWC) Carderock, and intended to represent material used in the construction of naval vessels. Details of each material selection are outlined below.

1. Steel

NSWC recommended standard plain carbon steel such as A36 be used for the experimentation. A36 is a typical structural steel used throughout the United States. Ultimately the steel selected was 1018 cold rolled steel. 1018 is nearly identical to A36 with one key difference. 1018 is cold rolled, whereas A36 is hot rolled. The hot rolling process results in a large amount of surface scale. The scale would have needed to be removed prior to use. The selection of cold rolled steel significantly reduced the surface preparation required for each sample. The steel was one eighth inch thick bar stock cut to length, and ordered from a local vendor.

2. Carbon Fiber Composite

The carbon fiber composite samples were constructed of TORAY T700CF carbon fiber weave with a DERAKANE 510–A40 vinyl-ester matrix. Again this is the carbon fiber composite used in several naval applications. The DERAKANE 510–A40 had to be cured and hardened. The ratios of the hardening chemicals, Methyl Ethyl Ketone Peroxide (MEKP) and 6% Cobalt Naphthenate (CoNap), as well as an accelerator, dimethylaniline (DMA), can be varied to control gel time of the resign based on ambient temperature. To ensure complete wetting of the carbon fiber the desired gel time was between forty five minutes and one hour. With an ambient temperature of seventy degrees Fahrenheit this was accomplished by using 1.25 weight percent MEKP, 0.2 weight percent CoNap and 0.03 weight percent DMA.

All carbon fiber samples were created using the Vacuum Assisted Resign Transfer Molding or VARTM technique. In this process the carbon fiber is laid up dry and a pressure differential, created by a vacuum, is used to draw the resin through the fiber layers. In this case a vacuum of approximately 635mm of mercury was used. Each carbon fiber panel was designed to be about 0.41 meters by 0.36 meters to provide 15 0.025 meter by 0.305 meter test specimens. This was also about the maximum size panel that could be created with the existing lab set up, and ultimately provided one set of seven test specimens for a carbon fiber to carbon fiber bond. Creating a test set from a single carbon fiber panel reduced variance that could have been introduced by using different carbon fiber panels.

After each carbon fiber panel was made it was taken to Integrated Composites, a local composite company, to be precisely cut on their water jet cutter. Each sample was allowed to cure a minimum of seven days prior to being bonded. This reduced the impact that a less than fully cured sample may have had on the results.

In order to ensure that the bonded surface fell on the neutral axis for bonds between different materials the stiffness of each material must be matched. Since steel and aluminum come in standard sizes the thickness of the carbon fiber composite was adjusted based on the thickness and Young's modulus of the steel and aluminum selected. In order to create a carbon fiber composite with the same stiffness of the one eighth inch thick 1018 steel, 13 layers of carbon fiber fabric were used for each sample. To match the stiffness of the one eighth inch think 5052 aluminum nine layers of carbon fiber fabric were used. Calculations used the below equation, h is equal to material thickness.

$$h_{comp} = h_{metal} * \sqrt[3]{\frac{E_{metal}}{E_{comp}}}$$

The values for Young's modulus that were used, are shown in Table 1. The value for carbon fiber was experimentally determined in lab.

Table 1.   Young's Modulus Values for Materials of Interest

Material	Young's Modulus (GPa)
1018 Steel	205 [19]
5052 Aluminum	70.3 [19]
Carbon Fiber Composite	52.402

3.   Aluminum

The aluminum selected for this study was 5052, a typical marine grade aluminum used in naval ship construction. The aluminum was ordered from a local supplier in a eighth inch thick four foot by eight-foot sheet, and cut into one inch by 12-inch strips using a power sheet metal shear.

4.   Pristine Carbon Nanotubes

A wide variety of carbon nanotubes are available for use. The nanotube selection was based on previous research conducted by Dr. Young Kwon and thesis student Susan Faulkner [2]. This research had success using concentric MWNTs with a diameter of 30nm +/- 15nm and a length of 5-20 μm. This size nanotube that was used is available as PD30L520 from Nanolab. In addition to the PD30L520 nanotubes, PD30L15 shorter nanotubes, PD15L520 smaller diameter nanotubes, BPD15L520 (a smaller diameter with a bamboo structure), and PD30L520 nanotubes with an attached carboxyl group, were also used. Further discussion of the carboxyl functionalized nanotube is below.

5.   Functionalized Carbon Nanotubes

Functionalization of the nanotubes was designed to enable better dispersion of the nanotubes in the adhesive. Believing that the adhesive had an amine based hardener, Dr. Craig Whitaker, from the Chemistry department at the United States Naval Academy, recommended using a carboxyl group to functionalize the nanotubes. The chemical interaction of the carboxyl group on the nanotubes with the amine in the adhesive should result in a better dispersion of the nanotubes.

The functionalization of the nanotubes was carried out by Dr. Whitaker as follows. The MWNTs (510 mg) were sonicated in 100 mL of mixed acid (3:1, concentrated H_2SO_4: concentrated HNO_3). Sonication of the MWNTs in H_2SO_4/HNO_3 (3:1) mixture increased the amount of carboxylation concurrent with sonication time up to 10 hours. The mixture was diluted with 800 mL distilled water and filtered. The solid was dried at room temperature and sonicated in a solution of 100 mL 4:1 sulfuric acid/hydrogen peroxide for 10 minutes. The reaction mixture was allowed to stand at room temperature for 1 hour. After dilution with 800 mL deionized water, the mixture was filtered through the 0.2 μm Teflon filter, washed with deionized water and then dried overnight at $80^{\circ}C$ in a vacuum oven. The process terminated the open ends and sidewall defect sites of the MWNTs with carboxylic acid groups (yield 460 mg). The loss of material is a result of the harsh reaction conditions. The molar percent carboxylation is between 8-10 percent [20].

Initial characterization of the nanotubes was conducted on an Infrared (IR) spectrometer by Dr. Whitaker. Additional characterization and comparison of the functionalized and pristine nanotubes was conducted using a Scanning Electron Microscope (SEM). Both SEM and IR characterization will be discussed later in this chapter.

6.   Adhesive Selection

Initially two adhesives were recommended and provided by NSCW Carderock for analysis. The recommendation of these specific adhesives was based on their current naval use. A single adhesive was selected for study to limit the scope of the research. That adhesive was selected based on higher Mode II energy release rate for the surface preparation techniques and specific materials selected for the research. The selected adhesive had higher values for both the steel-steel and steel-carbon fiber bonds. The adhesive selected was a two part epoxy engineered to maintain good strength characteristics while remaining flexible. The two parts were a resin and a hardener. Based on color and odor, the hardener was determined to be amine based.

B.   SAMPLE PREPARATION

Proper preparation of the surface is essential to provide a good consistent surface for the adhesive to bond to. All surfaces were prepared in accordance with manufacture recommendations. Details for the surface preparation of each material used are outlined below.

1.   Steel

Steel surfaces were initially cleaned with reagent grade acetone to remove grease and organic build up. The surface was then roughed up using glass beads in a sand blaster, and residual beads were removed with dry compressed air. Finally, the surface was wiped with a lint free rag to remove any remaining debris. All surfaces were bonded between several hours and one week of the glass bead abrasion to ensure a good clean surface was present. There was no difference between a sample which was bonded the same day as being abraded and one that was bonded several days after abrasion.

2.   Carbon Fiber

Carbon fiber composite samples were lightly sanded with 80 grit sand paper to expose some fiber and create a slightly roughed up surface for bonding. Following abrasion the surface was wiped with reagent grade acetone to remove any organic compounds, allowed to dry and wiped with a lint free cloth to remove any reaming debris. The surface was then bonded within a day.

3.   Aluminum

Aluminum surface preparation was accomplished with the adhesive manufacture's two part aluminum surface preparation solution. The first part was an acid etch solution which was allowed to stand on the aluminum surface for five minutes before being rinsed off. The surface was then allowed to air dry before application of the second part. The second part was a chromate solution which provided an oxidation resistant protective barrier on the surface of the aluminum. Again, the solution was allowed to stand for five minutes before being rinsed off. The surface then allowed to air

dry and the resulting surface was bonded within eight hours to ensure that a good surface for adhesion resulted.

C. ADHESIVE TECHINQUE

1. Mixing the Adhesive

All adhesive was mixed in small batches by weight ratio, 1.2:1, resin to hardener. Typical batch size was 11-15 grams. The resin was first weighed into a plastic cup and the hardener was added on top. The adhesive was then stirred by hand until it had a consistent color and smooth texture, about 3 minutes.

In cases in which nanotubes were added to the adhesive, the nanotubes were added after the resin, but prior to the hardener. Again the mixture was stirred by hand for three minutes until it was smooth and consistently colored.

2. Sample Assembly

Adhesive was applied to one of the two sample pieces using a plastic knife to get an even layer of adhesive on the surface. In cases where one piece was carbon fiber and one piece was steel the adhesive was applied to the steel piece. After application of the adhesive, a piece of Teflon film was folded on itself to create the crack tip. Generally the crack tip was located 0.075-0.09m from the end of the 0.305m specimen. This location ensured that a crack length of 0.05m and overall supported length of 0.22m were achievable for testing. The samples were then clamped using four evenly spaced one inch spring clamps to ensure consistent pressure across the bond surface. The clamps were left on overnight while the glue cured. The manufacture data shows that the adhesive obtained 90% of full strength after 24 hours of cure time. To reduce the variation from cure time, all samples were allowed to cure a minimum of 48 hours prior to testing.

D.   TESTING

In order to determine Mode II fracture toughness of each specimen a basic three point bending test was used. Figure 1 shows a sample set up. For most cases crack length "*a*" was set at 5cm and specimen length "2L" was 22cm. Specific data for each test can be found in Appendix A.
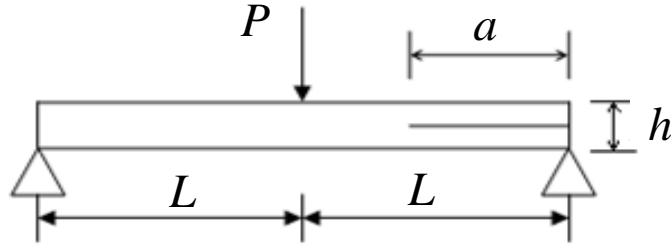
Figure 1.   Sample Geometry Under Three-Point Bending (2L = Length, h = Thickness, a = Initial Crack Length, P = Applied Load).

Testing was conducted on an Instron Tension/Compression Machine (Model Number: 4507/4500), with a 10kN load cell. Instron Series IX software was used to control the Instron and collect the data. A constant deflection rate of 1mm per minute was used for all tests. Further data analysis was conducted using a spreadsheet. Ultimately Mode II Fracture toughness, G_{II}, was calculated using the collected data and the below equation.

$$G_{II} = \frac{9a^2 P_c^2 C}{2b(2L^3 + 3a^3)}$$

For specimens composed of a carbon fiber piece (indicated by the yellow) and a steel piece (indicated by the red arrow) the specimen was tested with the carbon piece down as shown in Figure 2. The crack tip is indicated by the green arrow.
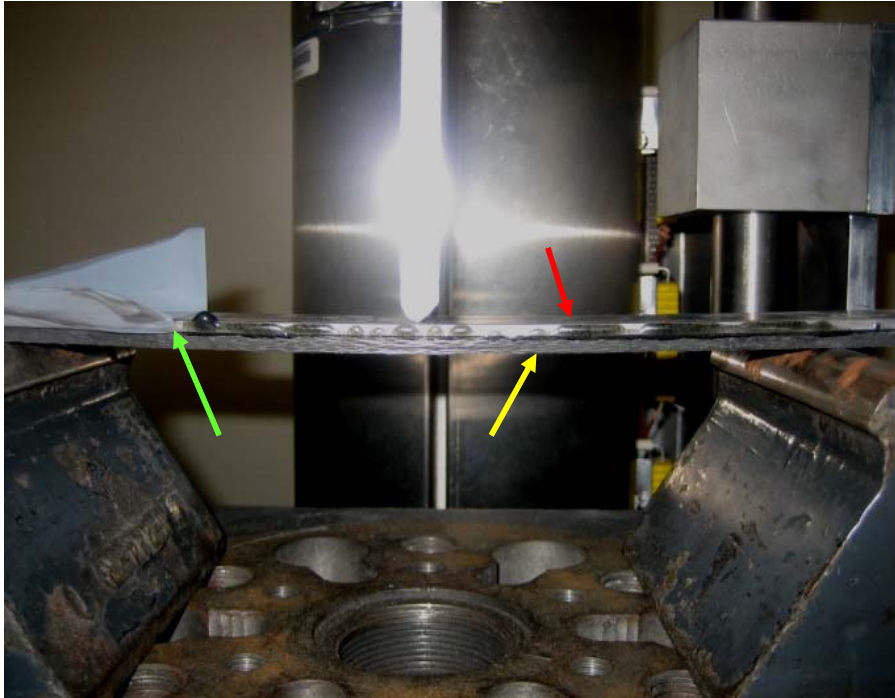
Figure 2.   Carbon Fiber-Steel Test Specimen showing Carbon Fiber down Orientation

E.   CARBON NANOTUBE CHARATERIZATION

Carbon nanotube characterization was performed using IR spectroscopy and SEM. The results of each of these techniques will be discussed below.

1. Infrared Spectroscopy

IR spectroscopy was performed by Dr. Craig Whitaker, hard copies of the spectra were provided with the functionalized nanotubes. Figure 3 is an IR spectrum of the pristine MWNT and Figure 4 is an IR spectrum of the carboxyl functionalized MWNTs.
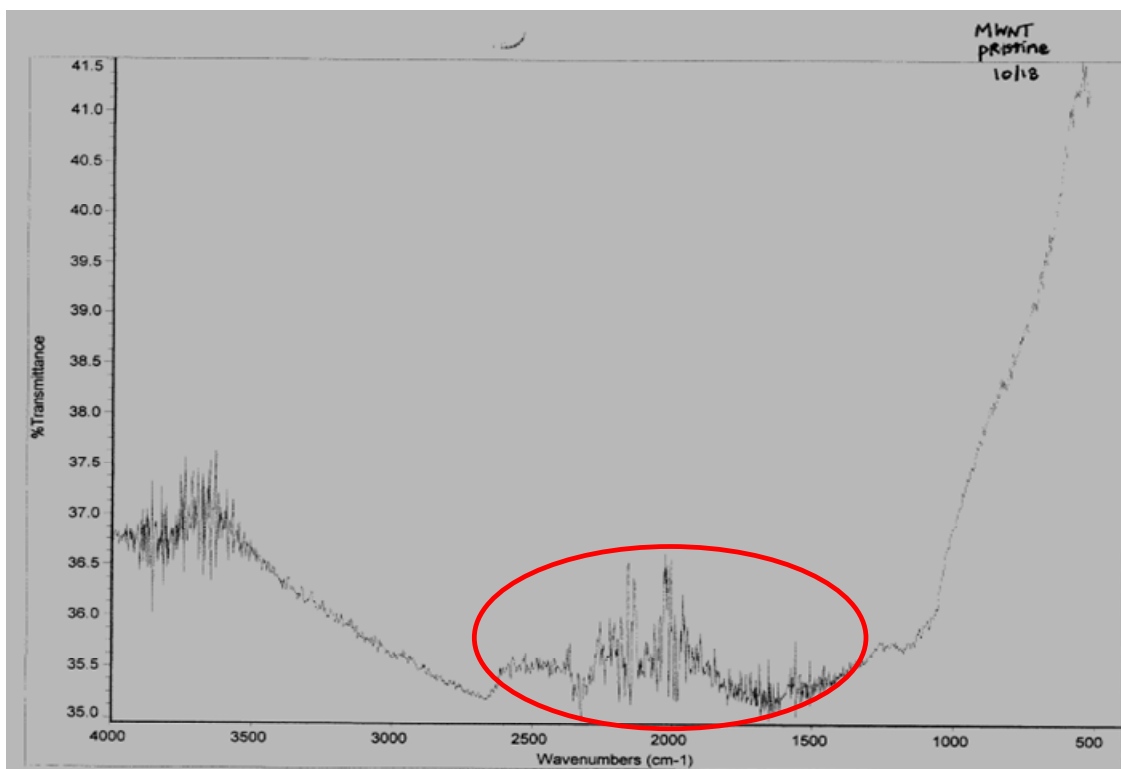
Figure 3.   IR Spectrum of Pristine MWNTs (From: Whitaker, 2009 [20])
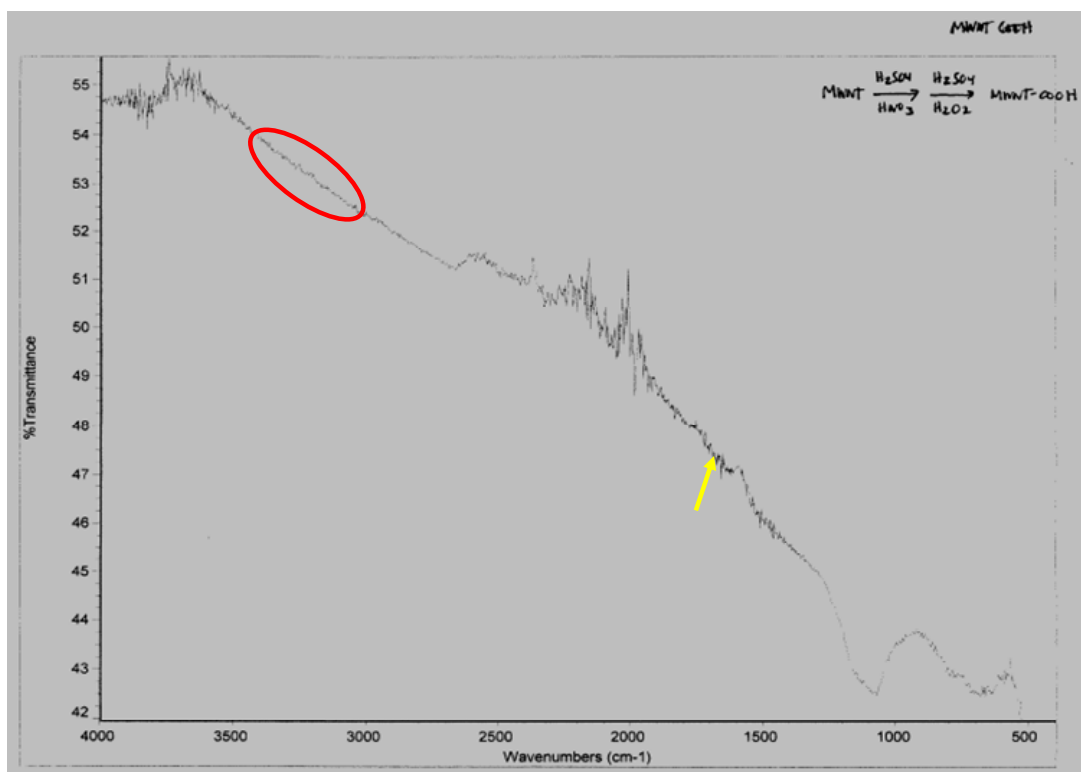
Figure 4.   IR Spectrum of COOH Functionalized MWNTs (From: Whitaker, 2009 [20])

In IR spectra a dip represents the absorption of a particular wave length of energy. The specific wavelength of the absorption is dependent on the various bonds that are present in the compound being analyzed.

The pristine MWNTs display broad absorption in the $1500-2500cm^{-1}$ region, indicated by the circle on Figure 3. This is the region in which carbon-carbon bonds occur, since MWNTs are composed entirely of carbon-carbon bonds we anticipate the spectrum looking as it does.

For the carboxyl functionalized MWNT absorption caused by a carbon double bonded to an oxygen and a carbon bonded to an alcohol (-OH) group were of interest since the pristine MWNT does not have these bonds. The absorption caused by a carbon-oxygen double bond will appear at $\sim1700cm^{-1}$. This area is indicated by an arrow on Figure 4 above. The alcohol group will appear as a relatively broad peak around $3000-3500cm^{-1}$. This area is indicated by a circle on Figure 4. Although both of these peak are present neither is prominent because of the relatively low carboxyl concentration, 8-10

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molar percent. The spectrometer used for the analysis did not have the ability to normalize the spectra to make these peaks visible. The spectra is however consistent with literature data [16].

The percent absorption or transmission from one sample to the next is not significant, only the shape and location of the absorption are significant. The fact that the pristine MWNT in general has a higher overall absorption is therefore not significant. The IR spectrums confirm that functionalization of the MWNTs occurred.

2. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was used for characterization of the carboxyl functionalized MWNTs and comparison to the pristine MWNTs. SEM was accomplished using the Carl Zeiss Neon 40 SmartSEM V05.03 Field Emission Scanning Electron Microscope. Beam energies of 2keV and 20keV were used. Samples were prepared by dispersing MWNTs in ethanol, water bath sonicated for 10 minutes, and then placed on a copper grid. Once on the copper grid the ethanol evaporated and the remaining carbon nanotubes on the grid were looked at with the SEM. Three distinct changes to the nanotubes were noted: shortening, wavy or rough surface and more dispersed. Each effect will be further discussed below.

a. Nanotube Shortening

The first significant observation was that the functionalized nanotubes were considerably shorter than the pristine ones. Figure 5 below shows that the length of the functionalized MWNTs was between 1-5μm. Figure 5 is representative of the functionalized nanotubes observed. The manufacturer reports that the PD30L520 nanotubes have a length of 5-20μm. Figure 6 below supports this claim when you consider that the distance between the arrows is 4μm and each of the six loops is about 0.5μm in diameter. This gives an overall length of about 12μm for the MWNT in Figure 6.
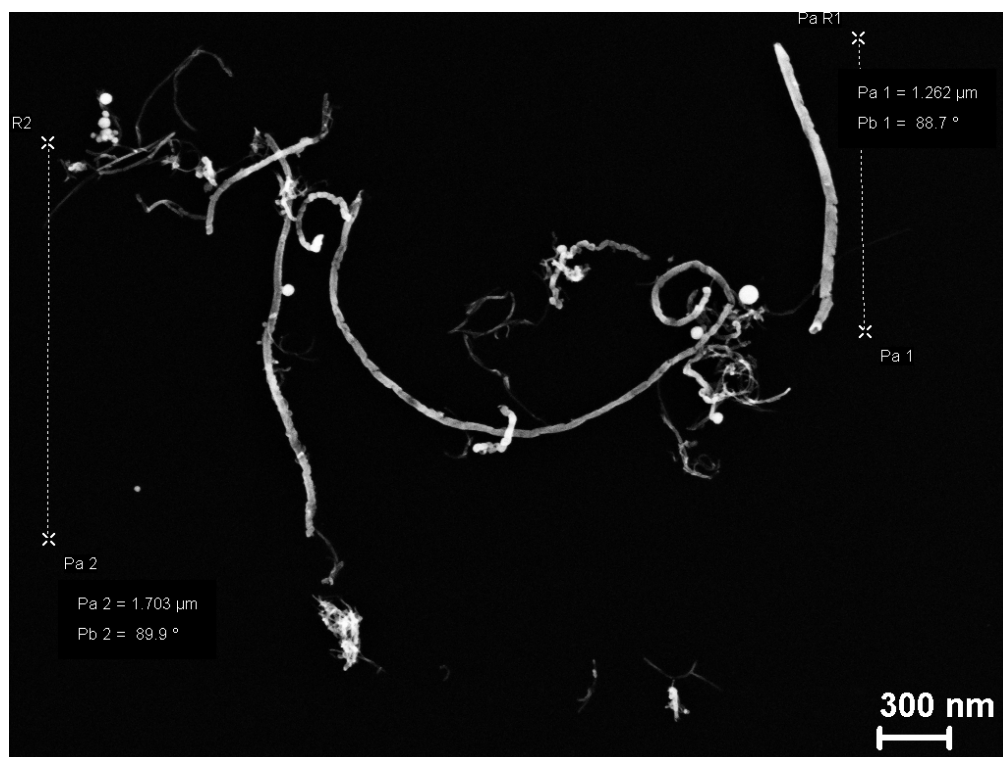
Figure 5.   Functionalized MWNT showing Shortened Length
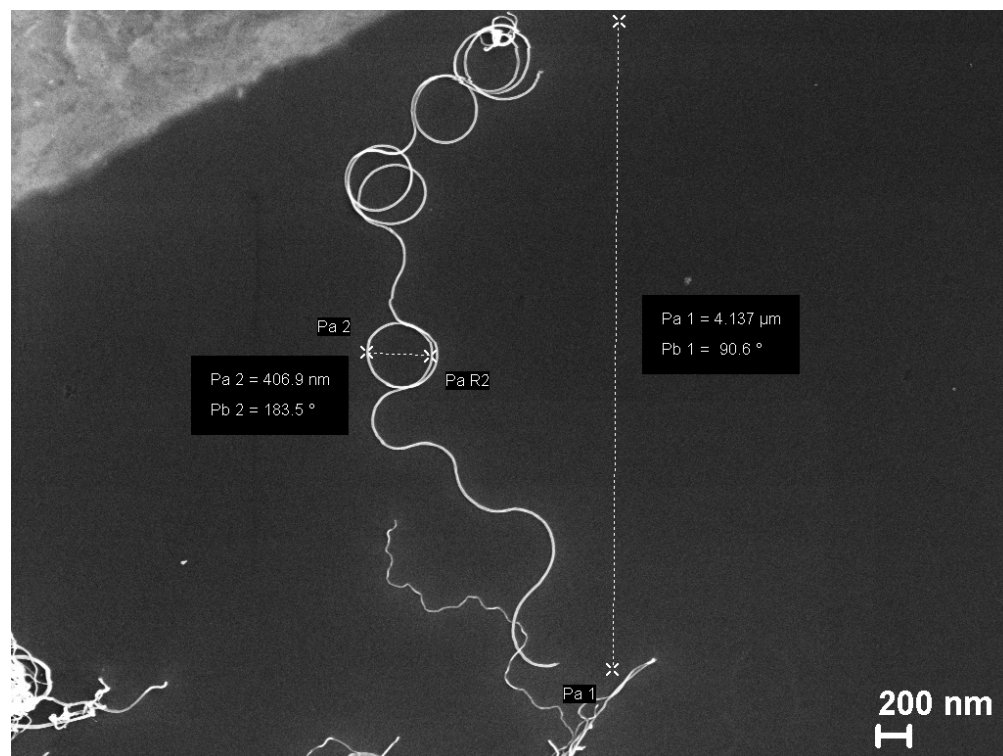
Figure 6.   Length of Pristine MWNT

b.   Wavy Nanotube Surface

In addition to the shortening of the nanotube, it was also noted that the surface of the functionalized nanotube was wavy, where the surface of the pristine nanotubes were straight and sharp. The wavy appearance of the functionalized nanotubes is caused by the carboxyl group causing additional scattering of the electron beam. Figures 7 and 8 are similar magnification. Figure 7 shows the wavy surface of a functionalized nanotube and figure 8 shows the straight surface of a pristine nanotube. The slightly rough surface of the pristine nanotubes is a result of vibration during the scan. Any small vibration, such as a voice, can cause distortion at such large magnifications.
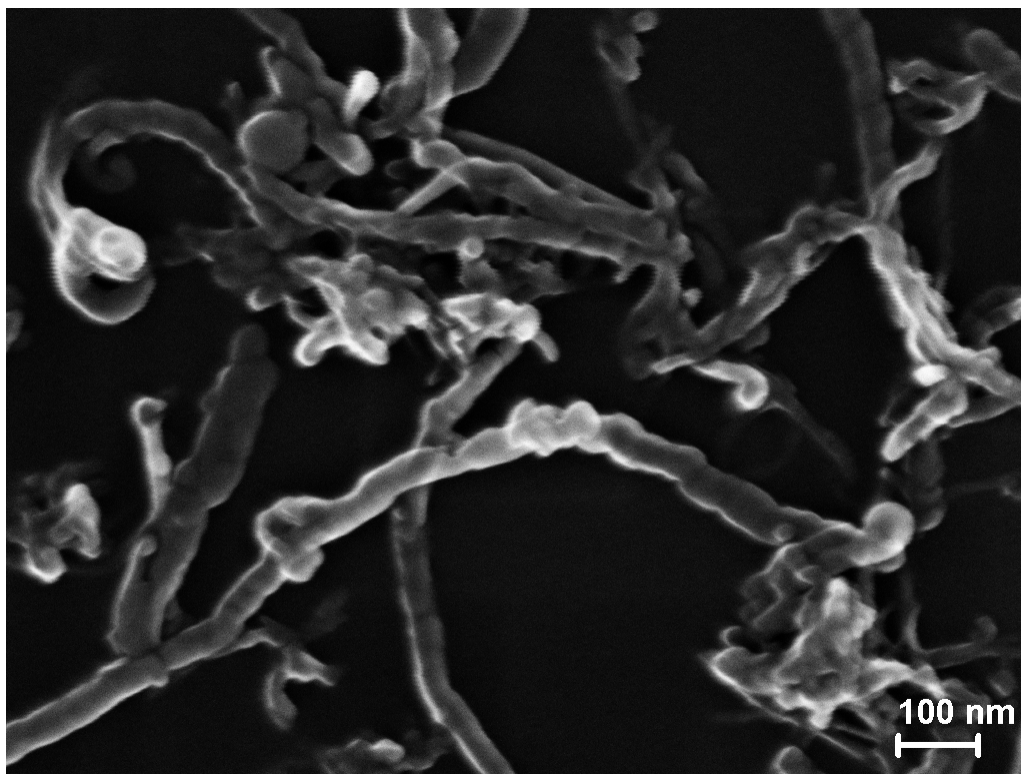
Figure 7.   Wavy Surface of Functionalized Nanotubes

Figure 8.   Straight Surface of Pristine Nanotube

c.   Dispersion Effect of Functionalization

The last observation was that the functionalized nanotubes tended to be spread out more. Although individual pristine nanotubes could be observed as in Figures 6 and 8, they were usually found in large bird nest like clumps as shown in Figure 9. In contrast, the functionalized nanotubes were found in much smaller and more disperse groups as shown in Figure 10.
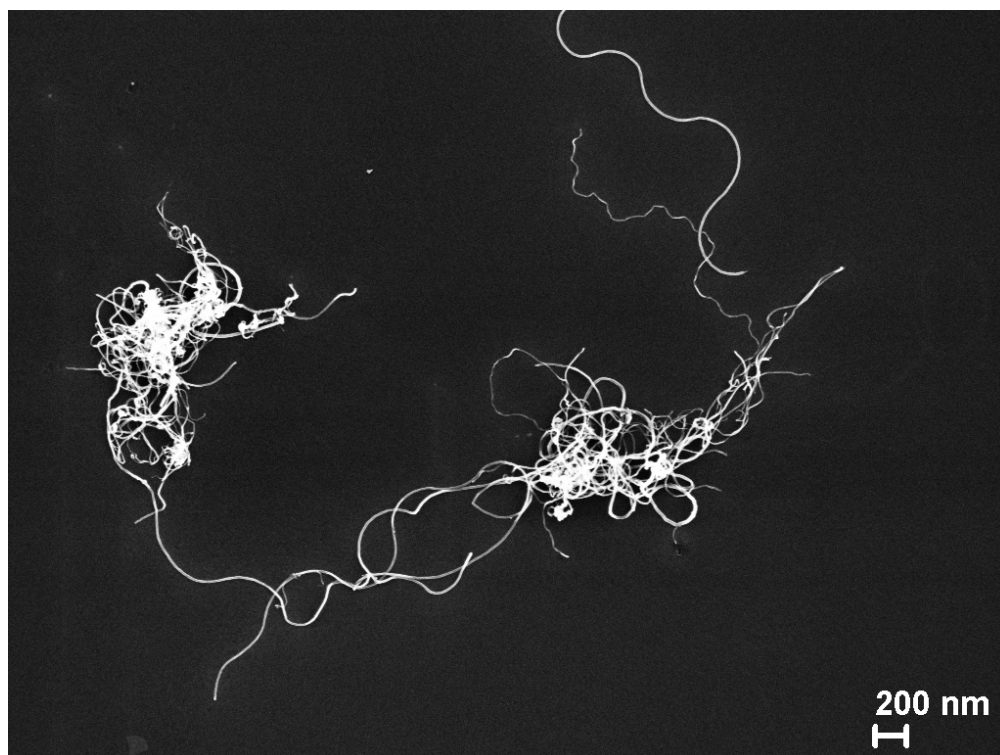
Figure 9.   Dispersion of Pristine Nanotubes
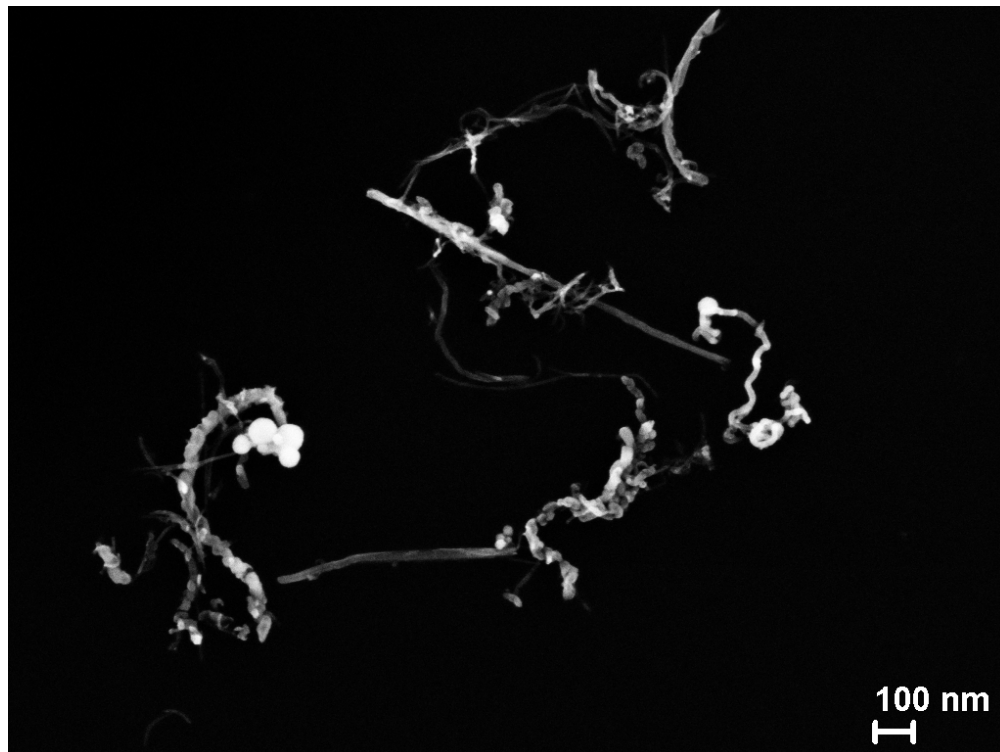
Figure 10.   Dispersion of Functionalized Nanotubes

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III. RESULTS AND DISCUSSION

A. STATISTICAL ANALYSIS AND REPORTING OF DATA

Following the collection of the data statistical analysis was conducted to determine the importance of the data collected and better understand the data's meaning. Although every attempt was made to reduce and eliminate variation from one sample to the next, the very nature of the materials and techniques being used resulted in variation between samples and sample sets. Some basic statistical techniques enabled it to be determined if the observed variation was a result of intentional changes or variation in the technique.

1. Confidence Intervals

The first statistical tool that was used was a confidence interval. Ninety percent confidence intervals were developed for each sample set. For a given set of data only the experimental mean is known. The actual mean remains unknown. A confidence interval establishes a range in which the true mean falls based on the experimental data. Confidence intervals are calculated from the standard deviation, the number of samples and the desired confidence for the interval. The standard deviation is a measure of the variation in a given sample set. A ninety percent confidence interval states that for a given set of data ninety percent of the time the true mean will fall within the range given by the interval.

B. ADHESIVE SELECTION

Initial testing was conducted to determine which of two recommended adhesives should be used. In order to determine the preferred adhesive steel-steel and steel carbon fiber bonds were tested with each adhesive. The first adhesive, West System's G-Flex, had a mode two energy release rate of 1.07E4 N/m for the steel-steel bond and 1.42E4 N/m for the steel-carbon fiber bond. The second adhesive, Pro-Set, had G_{II} of 1.23E3 N/m for the steel-steel bond and 1.95E3 N/m for the steel-carbon fiber bond. Data for

each specimen is available in appendix A. Based on these results the G-flex adhesive was used for the remainder of the testing.

C.   ADHESIVE WITH NO NANOTUBES

After making an adhesive selection, each joint type was tested with the selected adhesive with no CNT. The results of this testing are summarized in Figure 11. It was determined that failure for the adhesive without CNT occurred through the adhesive itself and was not dependant of the materials being adhered. This determination was based on the similar mode II energy release rate values determined for the steel-steel, carbon fiber-carbon fiber, and aluminum-aluminum bonds as shown in Figure 11. Visual inspection of the fracture surface also indicated that failure occurred through the adhesive.
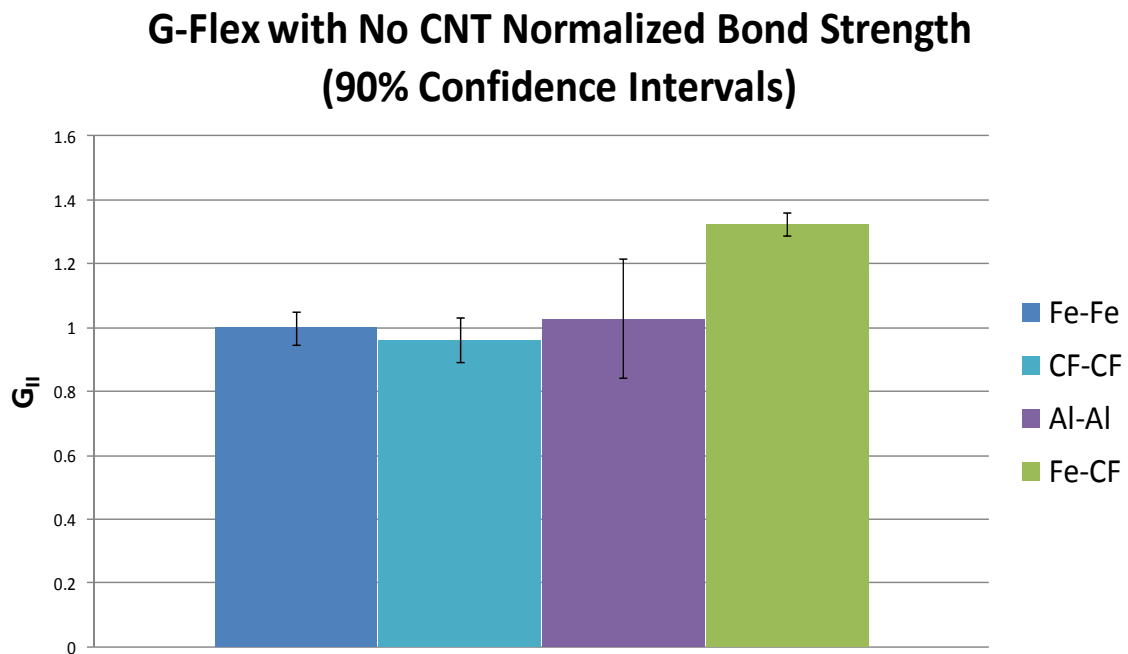
Figure 11.   Normalized Adhesive Energy Release Rate with no CNT

The higher mode II energy release rate of the steel to carbon fiber bond is a result of the initial crack being located off the neutral axis. Thus the energy release rate represented is actually a mixed mode energy release rate, not purely mode II energy release rate. The bond was located off neutral axis because only a discrete number of carbon fiber layers could be used to create a sample and thus only discrete values of

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carbon fiber thickness were available. Calculations indicated that 12.5 layers of carbon fiber should be used to produce a sample with the same stiffness as the 3.2mm thick steel sample. Since 13 layers of carbon fiber were used to construct the sample the stiffness did not exactly match and a mixed mode energy release rate resulted.

D.   ADHESIVE JOINT COMPARED TO CO-CURED SCARF JOINT

Next, it was determined that an adhesive joint was significantly stronger than a co-cured scarf joint. Figure 12 below shows that adhesive joints with and without the use of CNT were stronger than a similar co-cured joint. In fact they were approximately seven times stronger. The additional strength is the result of an epoxy adhesive being used verses a vinyl ester based resin that was used for the co-cured joint. Epoxies by their very nature are stronger than vinyl esters and the results are not unexpected. The data for the scarf joint is from Susan Faulkner's thesis work [2].
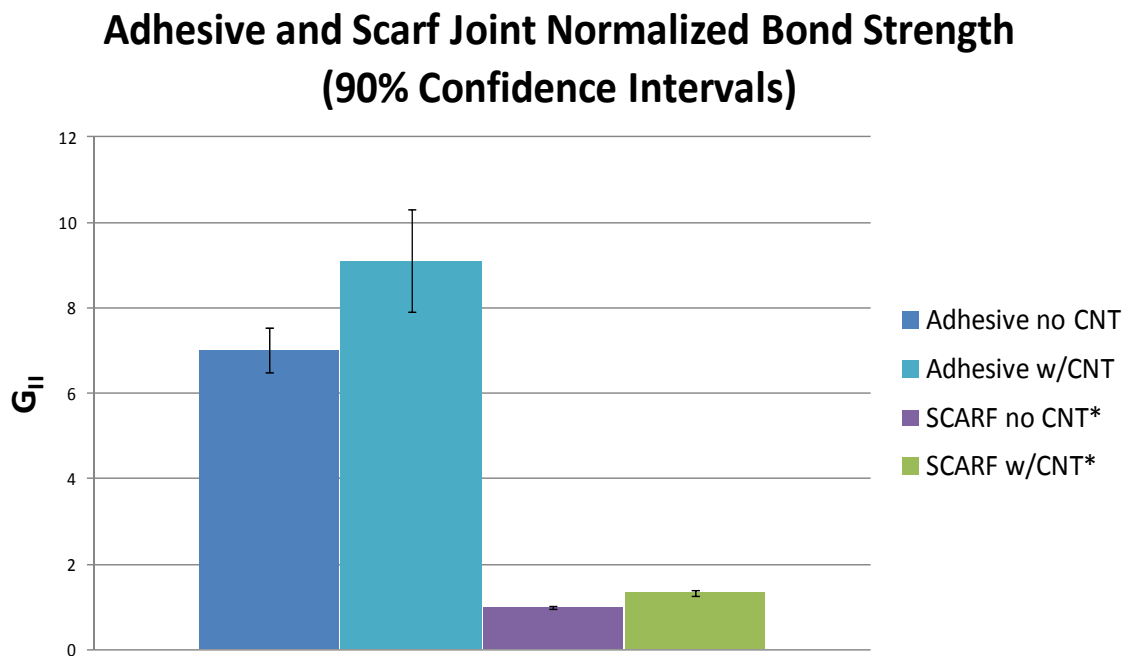
Figure 12.   Mode II Energy Release Rate of Adhesive Compared to Scarf Joint

E. STEEL TO CARBON FIBER JOINTS

Carbon fiber-steel joints were the next group of joints to be studied. The addition of pristine and carboxyl functionalized carbon nanotubes to the adhesive was studied. Various concentrations of pristine and functionalized MWNTs as well as a bamboo structure MWNT were used. Results are summarized in Figure 13 and experimental data is available in the Appendix.

Fe-CF Normalized Bond Strength (90% Confidence Intervals)
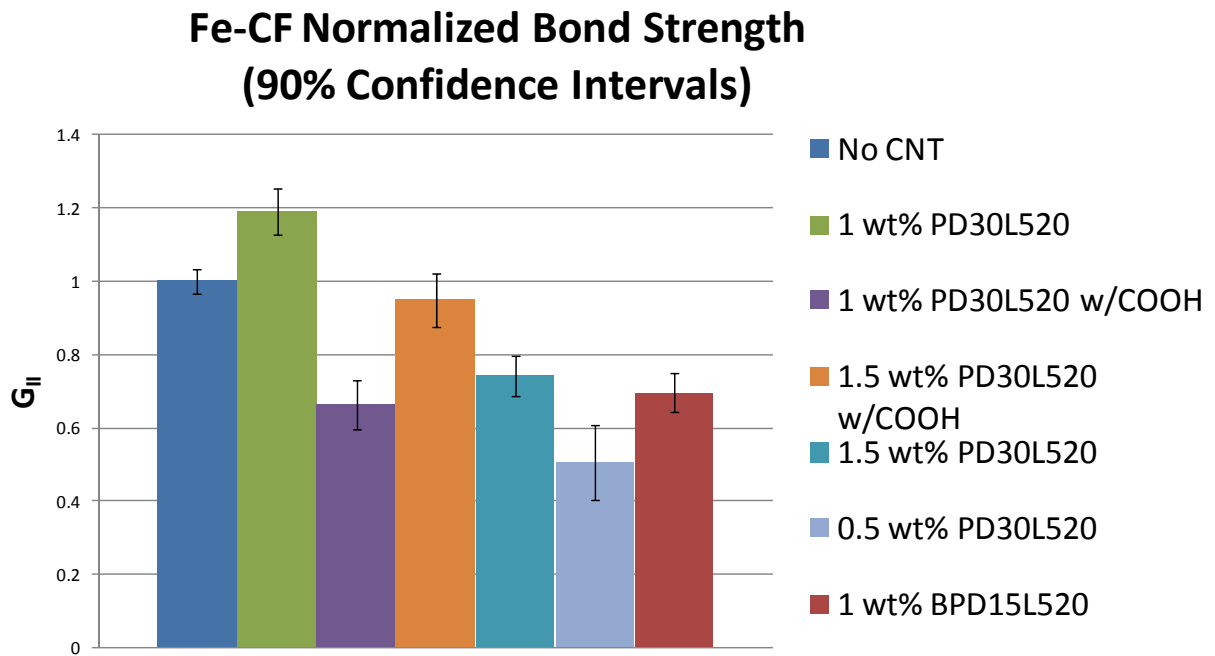
Figure 13.   Normalized Bond Strengths of Steel-Carbon Fiber Bonds

1.   Effect of Pristine MWNTs on Mode II Strain Energy Release Rate

The addition of one weight percent PD30L520 MWNTs increased mode II strain energy release rate by about 20%. With the inclusion of confidence intervals it was determined with 90% certainty that the G_{II} for the bond with MWNTs was higher than a bond without MWNTs. It was also observed that the failure path shifted from through the adhesive to the interface between the adhesive and the bonded material with the addition of MWNTs.

Furthermore, for the samples with larger G_{II} values more of the failure occurred mainly through the metal-adhesive interface. Samples with lower G_{II} values exhibited more failure through the carbon fiber-adhesive interface. Figure 14 below is the failure surface of a weaker bond and Figure 15 is the failure surface of a stronger bond. In both figures, the blue arrow depicts the location of the initial crack tip, the yellow arrow denotes areas of failure through the carbon fiber-adhesive interface, the green arrow denotes areas of failure through the steel-adhesive interface, and the red arrow indicates areas where sufficient contact was not made and thus bonding did not occur.
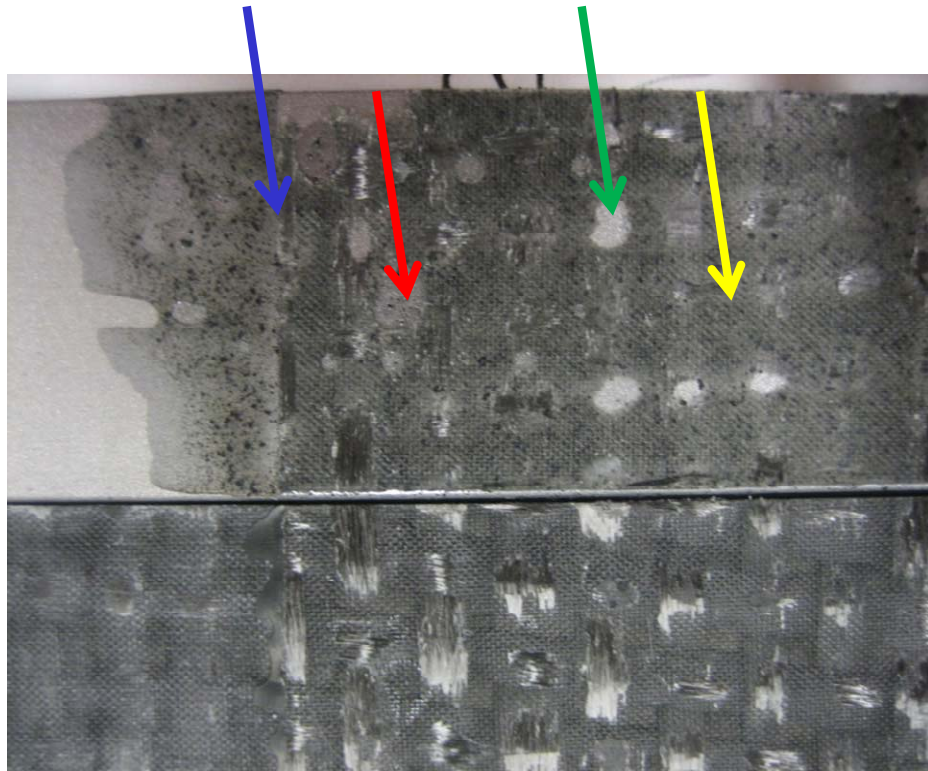
Figure 14.   Failure Surface of Weaker Steel-Carbon Fiber Bond with MWNTs
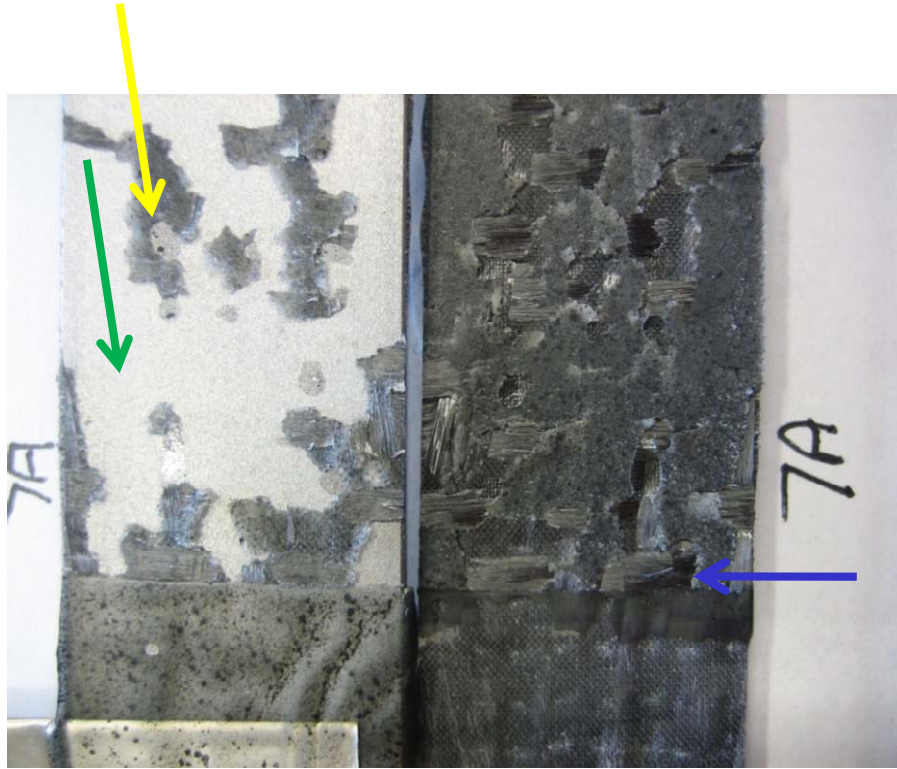
Figure 15.   Failure Surface of Stronger Steel-Carbon Fiber Bond with MWNTs

2.   Effect of Functionalized MWNTs on Mode II Strain Energy Release Rate

In the carbon fiber-steel bond, the addition of one weight percent carboxyl functionalized MWNTs resulted in G_{II} values 65% of the strength of the bond with no nanotubes. By increasing the weight percent of functionalized nanotubes to 1.5 weight percent the 90% confidence interval for the G_{II} overlapped with the 90% confidence interval for the joint with no nanotubes. The G_{II} value for both concentrations of functionalized nanotubes still remained below the G_{II} value for pristine nanotubes. The major reason is considered to be the shortened length of carboxyl functionalized MWNTs compared to the pristine MWNTs.

3.   Effect MWNTs Concentration on Mode II Strain Energy Release Rate

When the concentration of MWNTs was increased to 1.5 weight percent, the G_{II} value fell to about 70% of the bond with no nanotubes. Decreasing the weight percent of

MWNTs to 0.5% also reduced the G_{II} to 50% of the original strength. The failure occurred through the carbon fiber-adhesive interface and the amount of carbon fiber that was torn out was also reduced when the concentration of MWNTs was increased or decreased.

4. Effect of Using a Bamboo Structure MWNTs on Mode II Strain Energy Release Rate

The final different nanotube to be studied was a bamboo structured nanotube. The addition of one weight percent BPD15L520, a bamboo structure nanotube with diameter 15nm and length 5-20μm, resulted in a bond with 70% of the G_{II} of the original bond. Again the failure surface was generally through the carbon fiber-adhesive interface and there was little carbon fiber tear out noted on the failure surface.

F. CARBON FIBER-CARBON FIBER JOINTS

The final group of joints to be tested was the carbon fiber-carbon fiber joints. This test group looked at the effects of functionalization, concentration, nanotube length, and nanotube diameter. Results are summarized in Figure 16 and experimental data is available in the Appendix.
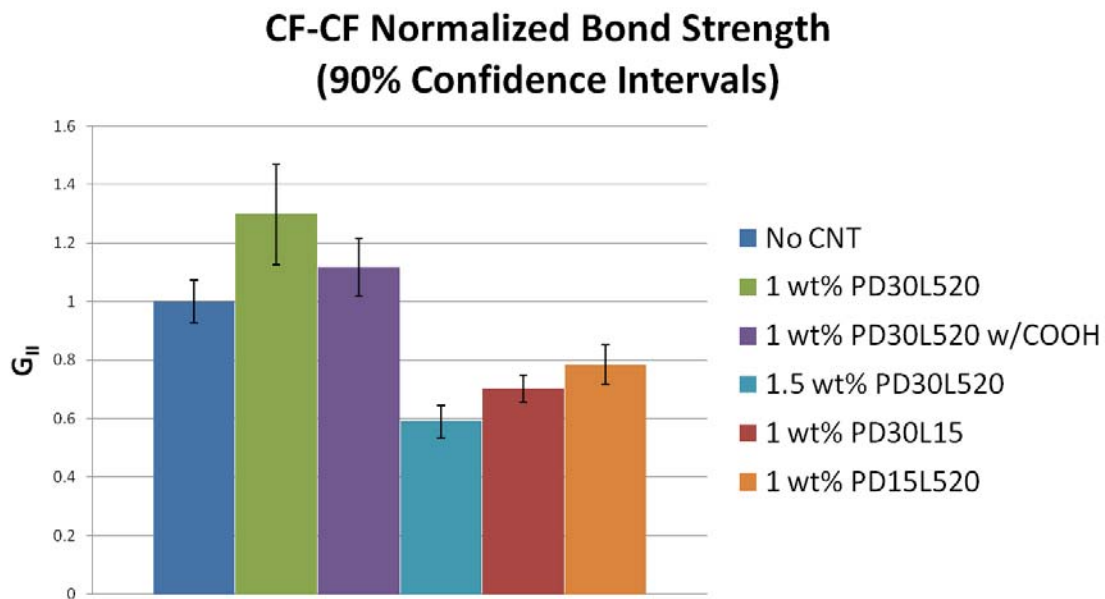
Figure 16.   Normalized Bond Strength of Carbon Fiber-Carbon Fiber Bonds

The addition of one weight percent pristine MWNTs resulted in a 30% increase in mode II strain energy release rate. Based on the statistical analysis it can be said with 90% certainty that the G_{II} of the samples with CNT are higher that the plain adhesive.

With the addition of one weight percent COOH functionalized MWNTs, the average G_{II} value increased by about 10%. However, based on the statistical analysis there is less then 90% confidence that the G_{II} for the functionalized nanotubes is greater then the G_{II} of the original sample. Additional tests could be conducted to show statistically that the functionalized nanotubes had a meaningful impact on joint strength.

As with the carbon fiber-steel joint, increasing the nanotube concentration to 1.5 weight percent resulted in a weaker bond. The resulting bond was only 60% as strong as the original bond with no nanotubes.

The addition of one weight percent PD30L15, a nanotube with a length of 1-5μm resulted in the G_{II} values that were only 70% of the original value. The addition of one weight percent PD15L520, a nanotube with a diameter of 15nm resulted in the G_{II} values that were only 80% of the original value.

IV. CONCLUSIONS AND RECOMMENDATIONS

A. ADHESIVE JOINT STRENGTH VERSUS CO-CURED SCARF JOINT

This research has shown that a carefully constructed adhesive joint can have mode II strain energy release rate that exceeds the strain energy release rate of a co-cured joint. This is an important discovery because co-cured joints are difficult to fabricate and require specially trained personnel and equipment to construct. This construction process limits the number of facilities that are able to construct such joints. In contrast adhesives are relatively simple to use and the adhesive process can be performed in a number of different settings. This is especially important in the repair of naval vessels. As more and more composite materials are used on board ship it is important that repair of composite structures be as simple as possible. This research demonstrates that adhesive is a viable ship repair option, which could be performed by ship's force with minimal training and very little specialized equipment.

Additional naval research and development needs to be conducted in the area of composite adhesive for use as a ship repair technique. Of specific concern with adhesives is the ability to ensure a good bond. Effort should be put into developing non-destructive techniques to verify adhesive joint integrity. Previously Bily has shown that CNTs could be used to track crack propagation in composite structures [21]. It is possible that CNTs could be used in a similar fashion to verify adhesive joint health. The development of such a technique would make adhesives a very attractive repair, and potentially construction, option for naval vessels.

B. STRENGTH GAIN FROM UNFUNCTIONALIZED CARBON NANOTUBES

It was demonstrated that the addition one weight percent PD30L520 MWNTs strengthened the steel-carbon fiber bond by 20% and the carbon fiber-carbon fiber bond by 30%. By examining the failure surfaces it was determined that a high strength steel-carbon fiber bond exhibited failure through the steel-adhesive interface, indicating that

the adhesive bonds more strongly to the carbon fiber than the steel. This is supported by the 30% strength increase in the carbon fiber-carbon fiber joint compared to the 20% gain in the steel carbon-fiber joint with the addition of MWNTs.

Further microscopic examination of the failure surface is required for confirmation, but it is suspected that the strongest bonds occur when the carbon nanotubes become entangled in the carbon fibers from the carbon fiber composite. This also explains the qualitative observation that the stronger carbon fiber-carbon fiber joints demonstrated greater carbon fiber tear out at the failure surface. In general, the greater the entanglement of the carbon nanotubes with the carbon fiber the more fiber tear out observed and the stronger the resulting joint will be. Since entanglement with the metallic surface was not possible the failure occurred through the metal adhesive interface. A direct comparison between G_{II} of carbon fiber-carbon fiber and carbon fiber-steel joints can not be made since the latter is actually a mixed mode G value because the initial crack was not located on the neutral axis.

1.   Effect of Carbon Nanotube Concentration

It was determined that there is an optimum concentration of nanotubes to maximize G_{II}. 0.5, 1.0 and 1.5 weight percent MWNTs were used for the carbon fiber-steel bond and it was determined that 1.0 weight percent had a positive effect while the other two concentrations degraded the bond. It is believed that if the concentration of carbon nanotubes is too high the nanotubes will begin to slip past one another and reduce the G_{II} value. If the concentration of nanotubes is too low there will not be sufficient entanglement with the carbon fiber to get the strength transfer from the nanotubes to the bulk material. Additional examination of the failure surface is required to determine the exact failure mechanism in each scenario. There is also additional work required to determine the ideal concentration of MWNTs to be used perhaps 1.25 weight percent would offer the greatest improvement.

2. Effect of Using Shorter Carbon Nanotubes

It was also demonstrated that the length of the nanotube is significant. For the carbon fiber—carbon fiber joints the addition of one weight percent PD30L15, a nanotube that is from 1-5μm in length, resulted in degradation to the bond strength. The resulting bond had only 70% of the strength of the bond with no nanotubes. It is possible, and in fact seems likely, that the shorter nanotubes may not be able to become entangled in the carbon fibers. As a result the nanotubes act more like a ball bearing and allow the adhesive to slip past the carbon fiber surface and thus lower the G_{II}.

Additional examination of the fracture surface is required to determine the exact failure mechanism. In addition to examining the fracture surface the concentration of MWNTs used should be varied. As shown previously there is some kind of optimum concentration to maximized bond strength. It is possible that a different concentration of the shorter nanotubes could have a positive effect on the bond strength.

3. Effect of Using Smaller Diameter Carbon Nanotubes

In addition to the concentration and length of the nanotube being used impacting the resulting strength the diameter of the nanotubes used also matters. The carbon fiber-carbon fiber joints were also tested with one weight percent PD15L520, a nanotube with diameter 5nm, was also tested. The resulting joint strength was 80% of the joint with no CNT. Two possible reason for the degradation are that the smaller diameter is not able to become entangled in the carbon fiber as well or the smaller diameter make the nanotubes less dense and thus an equivalent weight has a much larger volume. If the smaller diameter nanotube is not able to become entangled in the carbon fiber as well as the larger diameter then there is less opportunity for load transfer to the CNT and the resulting bond is not as strong. It is also possible that the volume of CNT added is as important as, or more important, than the weight of CNT added. Since the smaller diameter CNT is less dense, fewer nanotubes nested inside each other, a larger volume was added to the adhesive and they then had an adverse effect similar to the larger weight percent discussed above.

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Addition work is required to determine if all concentrations of smaller diameter MWNT degrade the bond. If bond strength improves when the amount added is decreased then the second explanation for degradation is correct. If additional CNT are required to improve strength than the idea that smaller nanotubes do not entangle as well as the larger diameter and thus a larger number are required for an improvement in strength then the first explanation may be correct. It is also possible that a combination of the two is the cause for reduced strength. If this is the case it is possible that this size nanotube will always degrade bond strength. Examination of the failure surface would also give insight into the failure mechanism.

## C.	ADVANTAGE OF FUNCTIONALIZED NANOTUBES

Carboxyl functionalized nanotubes were shown to improve the mode II strain energy release rate in a carbon fiber-carbon fiber joint by 10%, when one weight percent was added to the adhesive. Although a similar increase in strength was not observed in the carbon fiber-steel bond a positive trend was noted. Specifically the G_{II} value increased when the weight percent of nanotubes used was increased from 1.0 to 1.5. This was the only nanotube tested to show increased performance as the weight percent used was increased beyond 1.0. This indicates that the functional group enables a larger concentration of nanotubes to be added to the matrix without the degradation. It was also noted the joint strength of 1.5 weight percent functionalized nanotubes exceeded the strength of 1.5 weight percent pristine nanotubes.

### 1.	Better Dispersion

The SEM images of the functionalized and pristine nanotubes provide some insight as to why the weight percent of the functionalized nanotube can be increased with positive effect. From the SEM images we can see that the pristine nanotubes tend to wrap around each other and be found in birds nest like arrangements as noted in figure 9 above. In contrast the functionalized nanotubes tended to be more dispersed and not clumped together as shown in figure 10 above.

The dispersion is a result of the functionalization. The nanotubes were first suspended in an ethanol solution before being placed on the carbon grid for analysis in the SEM. It is important to consider the chemistry that occurred in the solution because it is similar the chemistry in the adhesive's amine based hardener. The carboxyl function group is drawn to the ethanol since both have an OH^- group present. The pristine nanotubes do not have any functionalization on their surface and thus are not drawn into the solvent. They are only mechanically agitated free from their clumps by the sonication.

In a similar way, the functionalized nanotubes are chemically attracted to the adhesive and thus distribute better throughout the adhesive. As a result of the better dispersion a larger concentration of the functionalized nanotubes can be added before they begin to act like mini ball bearings and slip past each other to reduce G_{II} values.

Further microscopic examination of the adhesive matrix is required to confirm that the dispersion of the functionalized nanotubes is better than pristine ones in the adhesive. Basic principles of chemistry indicate that this should be the case. Additional testing needs to be done to determine what the ideal concentration of functionalized nanotubes is. There is a very good chance that with a higher weight percent the strength could exceed that of the pristine nanotubes for the carbon fiber-carbon fiber joint and possible for the carbon fiber-steel joint as well.

2. Loss of Strength Due to Shortening of Nanotubes During Functionalization

The SEM also offered insight to why the functionalized nanotubes did not improve the strength of the bond as much as the pristine ones. As previously shown the length of the nanotubes has a significant impact on the resulting joint strength. If the nanotubes are too short there is not a strength gain. The SEM showed that the nanotubes were significantly shortened during the functionalization process. Figures 5 and 6 above show the decrease in length of the nanotubes. Typical nanotube length after functionalization was 1-2μm. For the carbon fiber-carbon fiber joint the short pristine nanotubes produced a joint with 70% of the strength of the joint with no nanotubes. By

contrast the short functionalized nanotube produced a joint that was 10% stronger than the joint with no nanotubes or 50% stronger than the joint with short pristine nanotubes. From this standpoint the functionalized nanotube had significant improvement over a similar sized nanotube with no functionalization.

The next step is to use functionalized nanotubes that are not shortened. Starting the functionalization process with longer nanotubes or changing the reaction conditions or times could produce such nanotubes. Once longer functionalized nanotubes are obtained additional experimentation will be required to determine the ideal concentration of nanotubes that should be used and the resulting joint strength.

3.   Ability to Fine Tune Functional Group to Specific Needs

This research has shown that there is great potential for using the carboxyl functionalized nanotubes to strengthen an epoxy adhesive. Despite the significant shortening of the nanotube by the functionalization process there was still an improvement in the joint strength. Other nanotubes of similar length degraded joint strength. It was also shown that the functional group enabled a larger concentration of nanotubes to be incorporated into the adhesive without a detrimental effect. The full benefit of high nanotube incorporation was not investigated, but in addition to improvement of mechanical properties it may improve electrical characteristics and enable development of a non-destructive testing technique. To maximize the benefit of using functionalized nanotubes more thought needs to be given to what the functional group should do.

For the purposes of this research the carboxyl group was selected because of ease of functionalization and the flexibility that it provides. Without knowing specific details about the adhesive the carboxyl group represented a best chance at good interaction with the adhesive. Ideally the specific characteristics of the adhesive of interest would be known and the functional group could be tailored to chemically react and harden into the adhesive matrix. Careful tailoring of the functional group may enable the nanotubes to chemically bond into the adhesive matrix. Chemical bonding of the nanotubes in the

adhesive matrix would enable better transfer of the nanotubes strength to the adhesive matrix and may result in a significantly stronger joint.

D.   SUMMARY

This research has shown that carbon nanotubes can be used to improve the mode II energy release rate of epoxy adhesives. However not all concentrations, sizes, length and structure of nanotubes improve joint strength. In fact many can degrade joint strength and they have an ideal concentration that they should be used in. The research has also shown that functionalized carbon nanotubes can also be used to improve joint strength despite their shorter length. This strength gain is a result of the improved dispersion of the nanotube in the adhesive matrix that the functional group provides. This research focused on using simple techniques that could be duplicated in a wide variety of environments to facilitate repair of composite structures on naval vessels. Noting that the dispersion of the nanotubes is important to get the full advantage of their inclusion, additional research should be done to determine the best technique for dispersion. Ideally the nanotubes could be functionalized and then incorporated into one of the parts of a multipart epoxy. This is perhaps where the future of nanocomposites and nanoadhesives lie.

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APPENDIX: TABULATED EXPERIMENTAL DATA

Adhesive Strength

G-Flex Sample	Joint	Adhesive	CNT	G-Value (N/m)								90% Confidence Interval (+/-)
				A	B	C	D	E	F	G	Avg	
2	Fe-Fe	G-flex	None	1.10E+04	1.06E+04	1.08E+04	1.04E+04	1.21E+04	9.09E+03	1.11E+04	1.07E+04	562.6131014
4	Fe-CF	G-flex	None	1.53E+04	1.40E+04	1.40E+04	1.38E+04	1.40E+04			1.42E+04	383.4150633
8	Al-Al	G-flex	None	1.30E+04	9.37E+03	8.81E+03	8.92E+03	8.27E+03	1.73E+04	1.17E+04	1.10E+04	2009.928118
12	CF-CF	G-flex	None	9.69E+03	1.26E+04	1.00E+04	9.53E+03	1.13E+04	9.15E+03	9.93E+03	1.03E+04	761.5439328

Adhesive Joint Versus Co-Cured Joint Strength

CF-CF Sample	Joint	Adhesive	CNT	G-Value (N/m)								90% Confidence Interval (+/-)
				A	B	C	D	E	F	G	Avg	
12	CF-CF	G-flex	None	9.69E+03	1.26E+04	1.00E+04	9.53E+03	1.13E+04	9.15E+03	9.93E+03	1.03E+04	761.5439328
13	CF-CF	G-flex	1 wt% PD30L520	1.07E+04	1.86E+04	1.29E+04	1.06E+04	1.18E+04	1.44E+04	1.49E+04	1.34E+04	1768.318634
	CF-CF	Co-Cured	None	1.50E+03	1.38E+03	1.48E+03	1.51E+03	1.49E+03			1.47E+03	38.71525634
	CF-CF	Co-Cured	7.5 g/m2	2.00E+03	1.78E+03	1.90E+03	2.08E+03				1.94E+03	106.5986984

Carbon Fiber - Steel Joints

FE-CF Sample	Joint	Adhesive	CNT	G-Value (N/m)								90% Confidence Interval (+/-)
				A	B	C	D	E	F	G	Avg	
4	Fe-CF	G-flex	None	1.53E+04	1.40E+04	1.40E+04	1.38E+04	1.40E+04			1.42E+04	453.6628209
5	Fe-CF	Proset	None	9.27E+02	4.04E+03	1.18E+03	1.81E+03	1.78E+03			1.95E+03	766.3929563
6	Fe-CF	G-flex	Surface 7.5g/m2	6.77E+03	6.96E+03	5.70E+03	1.05E+04	1.65E+04	1.20E+04	8.94E+03	9.63E+03	2337.225612
7	Fe-CF	G-flex	1 wt% PD30L520	1.72E+04	1.86E+04	1.70E+04	1.01E+04*	1.64E+04	1.29E+04*	1.56E+04	1.69E+04	901.5513737
9	Fe-CF	G-flex	1 wt% CheapTubes	1.15E+04	7.67E+03	1.28E+04	7.81E+03	1.06E+04	8.51E+03	1.13E+04	1.00E+04	1261.002042
10	Fe-CF	G-flex	0.5 wt% PD30L520	7.04E+03	6.90E+03	4.17E+03	6.82E+03	9.71E+03	5.06E+03	1.06E+04	7.19E+03	1432.775185
15	Fe-CF	G-Flex	1.5 wt% PD30L520	1.10E+04	1.09E+04	9.62E+03	1.20E+04	1.21E+04	9.32E+03	8.95E+03	1.06E+04	791.9741974
19	Fe-CF	G-Flex	1 wt% PD30L520 w/COOH	1.03E+04	7.81E+03	7.62E+03	1.09E+04	8.86E+03	8.87E+03	1.15E+04	9.42E+03	943.8357729
20	Fe-CF	G-Flex	1 wt% BPD15L520	8.89E+03	9.86E+03	1.04E+04	7.67E+03	1.11E+04	1.07E+04	1.08E+04	9.90E+03	759.2949229
21	Fe-CF	G-Flex	1.5 wt% PD30L520 w/COOH	1.21E+04	1.39E+04	1.05E+04	1.40E+04	1.39E+04	1.48E+04	1.53E+04	1.35E+04	1038.541001

*Data points highlighted in yellow were not included in the average value because of adhesive voids near the crack tip.

Carbon Fiber – Carbon Fiber Joint Strength

CF-CF Sample	Joint	Adhesive	CNT	G-Value (N/m)								90% Confidence Interval (+/-)
				A	B	C	D	E	F	G	Avg	
12	CF-CF	G-flex	None	9.69E+03	1.26E+04	1.00E+04	9.53E+03	1.13E+04	9.15E+03	9.93E+03	1.03E+04	761.5439328
13	CF-CF	G-flex	1 wt% PD30L520	1.07E+04	1.86E+04	1.29E+04	1.06E+04	1.18E+04	1.44E+04	1.49E+04	1.34E+04	1768.318634
14	CF-CF	G-Flex	1.5 wt% PD30L520	7.18E+03	5.08E+03	5.93E+03	7.55E+03	5.69E+03	5.93E+03	5.18E+03	6.08E+03	588.8728624
16	CF-CF	G-Flex	1 wt% PD30L520 w/COOH	1.22E+04	1.03E+04	9.43E+03	1.06E+04	1.18E+04	1.45E+04	1.18E+04	1.15E+04	1017.823429
17	CF-CF	G-Flex	1 wt% PD30L15	7.68E+03	6.32E+03	8.18E+03	6.89E+03	6.66E+03	6.88E+03	8.15E+03	7.25E+03	464.7207675
18	CF-CF	G-Flex	1 wt% PD15L520	8.61E+03	1.01E+04	7.68E+03	7.37E+03	8.88E+03	7.40E+03	6.69E+03	8.10E+03	711.6549872

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